

CLAIMS

1. Method for preparing a suspension of a silicic particulate filler, in a silicone material (SM) comprising:

5 > *SM₁polyaddition*:

- at least one type A polyorganosiloxane POS carrying alkenyl crosslinking functional groups Fa capable of reacting with the crosslinking functional groups Fb (SiH) of at least one B type POS, this A POS being taken alone or as a mixture with at least one nonreactive (E) POS;
- and at least one B type POS carrying crosslinking functional groups Fb (SiH) capable of reacting with the alkenyl crosslinking functional groups Fa of the A POS(s);

10 o and/or *SM₂polycondensation*:

- at least one C type POS carrying hydroxyl crosslinking functional groups Fc and/or OR functional groups (R = C₁-C₃₀ alkyl, C₂-C₃₀ alkenyl, aryl, which are optionally substituted (preferably halogenated)) precursor of the functional groups Fc', these crosslinking functional groups Fc being capable of reacting with crosslinking functional groups Fc of this C POS or of other C POSs, and with crosslinking functional groups of at least one crosslinking agent D, this C POS being taken alone or as a

mixture with at least one nonreactive (E) POS;

➤ and/or SM_3 polydehydrogenocondensation:

- at least one C' type POS carrying hydroxyl crosslinking functional groups Fc' and/or OR' functional groups ($R' = C_1-C_{30}$ alkyl, C_2-C_{30} alkenyl, aryl, which are optionally substituted (preferably halogenated)) precursor of the functional groups Fc' , these crosslinking functional groups Fc' being capable of reacting with other crosslinking functional groups Fb' (SiH) of at least one B' type POS, this C' POS being taken alone or as a mixture with at least one nonreactive (E) POS;
- and at least one B' type POS carrying crosslinking functional groups Fb' (SiH) capable of reacting with the crosslinking functional groups Fb' OH or OR' of the C' POS(s);

➤ and/or SM_4 :

- or at least one nonreactive (E) POS;
- this suspension being capable of being used in particular for producing compositions which can be crosslinked by polyaddition and/or by polycondensation and/or by dehydrogenocondensation or antifoam silicone compositions;
- this method being of the type in which an aqueous suspension of silicic particulate filler is made hydrophobic by treating with at least one halogenated

reagent, this treatment comprising a transfer of the silica made hydrophobic into a nonaqueous phase and at least one step for at least partial removal of water,

5 characterized in that:

a) an aqueous silica suspension is prepared or used which comprises:

~ silica,

~ water which is optionally acidified,

10 ~ at least one hydrogen bond stabilizer/initiator,

b) optionally, part of the silicone material SM is incorporated into the aqueous silica suspension obtained at the end of step a);

15 c) hydrophobic units formed by $\equiv\text{Si}-(\text{R}^c)_1 \text{ to } 3$ with $\text{R}^c =$ hydrogeno, $\text{C}_1\text{-C}_{30}$ alkyl, $\text{C}_2\text{-C}_{30}$ alkenyl, aryl, these groups R^c being optionally substituted (preferably halogenated), are grafted onto the silica by
20 exposing this silica to halosilanes that are precursors of these units and by allowing the reaction to proceed, preferably while stirring the whole, optionally in the hot state;

25 d) the procedure is carried out such that the transfer of the silica grafted by hydrophobic units, from the aqueous phase to the

nonaqueous phase, is carried out;

e) optionally, at least part of the aqueous phase and of the reaction by-products is drawn off;

5 f) the medium is cooled if necessary;

g) optionally, the residual acidity of the nonaqueous phase is washed off;

h) the totality or the remainder of the silicone material *SM* is mixed with the filler
10 which is now hydrophobic;

i) the residual water is evaporated off;

j) and an oil is recovered which consists of a hydrophobic particulate filler suspension in a crosslinkable silicone material,
15 preferably without ever passing via a dried hydrophobic silica.

2. Method according to Claim 1, characterized in that the pH of this suspension is ≤ 2 , preferably ≤ 1 , at least during step a).

20 3. Method according to Claim 1, characterized in that at least one precursor of silicone resin, preferably a silicate, and still more preferably a sodium silicate, is used in step a).

4. Method according to Claim 1,
25 characterized in that functional units other than hydrophobic units are grafted onto silica by exposing it to halosilane precursors of these functional grafts,

the functions which can be given to the silica by these units being preferably those in the group comprising the following functions: bactericidal, bacteriostatic, chromophoric, fluorescence, antifouling, and
5 combinations thereof.

5. Method according to Claim 1, characterized in that there are chosen one or more precipitated silicas whose BET specific surface area is between 50 and 400 m²/g and mixing conditions such that
10 the dynamic viscosity at 25°C of the suspension is less than or equal to 300 Pa.s, preferably less than or equal to 150 Pa.s.

6. Method according to any one of Claims 1 to 5, characterized in that the hydrogen bond
15 stabilizer/initiator is chosen from organic solvents, preferably from the group comprising alcohols, ketones, amides, alkanes and mixtures thereof.

7. Method according to any one of Claims 1 to 6, characterized in that the acidification of the
20 aqueous suspension (aqueous phase) is carried out using an acid, preferably an inorganic acid, and still more preferably an acid is chosen from the group comprising: HCl, H₂SO₄, H₃PO₄ and mixtures thereof.

8. Method according to any one of Claims 1 to 7, characterized in that the silicone material SM
25 comprises at least one oligoorganosiloxane, preferably a diorganosiloxane, and still more preferably

hexamethyldisiloxane (M_2).

9. Method according to any one of Claims 1 to 6, characterized in that the precursor of hydrophobic units is an alkylhalosilane, preferably an alkylchlorosilane, and still more preferably a methylchlorosilane.

10. Method according to any one of Claims 1 to 9, characterized in that a precipitated silica powder is used and in that the following operations are carried out:

- the relevant products are introduced into the stirred preparation vessel in the following order:
 - o the aqueous silica suspension, optionally in several fractions, the hydrogen bond stabilizer/initiator - preferably consisting of isopropyl alcohol, optionally an acid -, preferably HCl -;
 - o a precursor of hydrophobic units: $-\text{Si}-(\text{R}^c)_{1 \text{ to } 3}$ with $\text{R}^c = \text{C}_1\text{-C}_{30}$ alkyl or a $\text{C}_2\text{-C}_{30}$ alkenyl - preferably $(\text{CH}_3)_3\text{SiCl-}$;
 - o part of the SM consisting of at least one oligoorganosiloxane - preferably hexamethyldisiloxane (M_2)-;
- the medium is heated to a temperature in the region of the reflux temperature of the hydrogen bond stabilizer/initiator - preferably that of isopropyl alcohol between 70 and 80°C;

- the medium is optionally cooled;
- the aqueous phase is separated from the nonaqueous phase - preferably by decantation -;
- the nonaqueous phase is removed;
- 5 • optionally at least once, this nonaqueous phase is washed with an aqueous liquid and then the aqueous washing phase is removed;
- the optionally washed, nonaqueous silicone phase is mixed with all or the remainder of the silicone material *SM*, with the silica now hydrophobic, this
- 10 *SM* preferably comprising at least one polyorgano-siloxane POS;
- an oily suspension of hydrophobic particulate silicic filler is recovered in a crosslinkable
- 15 silicone material *SM*.

11. Method according to any one of Claims 1 to 10, characterized in that the various ingredients are used in the following proportions (parts by dry weight for all that is not water):

- 20 - silica: 100;
- acid (e.g. HCl): 20 to 60, preferably from 30 to 50;
- precursor of $-\text{Si}-(\text{R}^c)_{1 \text{ to } 3}$ (e.g. $(\text{CH}_3)_3\text{SiCl}$), 5 to 500, preferably from 10 to 200;
- H bond stabilizer/initiator (e.g. isopropanol): 0 to
- 25 20, preferably from 1 to 10;
- *SM* oil: 40 to 2 000, consisting exclusively or otherwise of oligoorganosiloxane - preferably of M_2 ;

- water: 2 to 8 000, preferably 200 to 1 000.

12. Method according to any one of Claims 1 to 11, characterized in that the silica used is mainly in the form of a slurry of precipitated silica(s).

13. Method according to any one of Claims 1 to 12, characterized in that a polyaddition SM is used which contains:

- at least one reactive silicone oil A POS whose crosslinking functional groups Fa are alkenyl - preferably vinyl - functional groups,

this A POS:

- comprising at least two Si-Fa groups per molecule, preferably each situated at one end of the chain,
- and having a dynamic viscosity at 25°C of less than or equal to 250 Pa.s, preferably 100 Pa.s and still more preferably 10 Pa.s,

this A POS being intended to react with the B POS,

- at least one reactive silicone oil B POS, whose crosslinking functional groups Fb are hydrogen functional groups, this B POS comprising at least two groups Si-H per molecule (preferably at least three when the A POS comprises only two Si-Vi groups per molecule), these Si-H groups being advantageously

situated in the chain,

- and/or at least one nonreactive E POS;

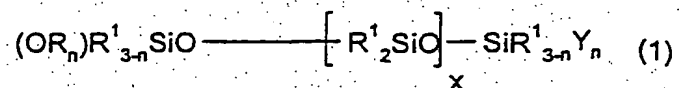
and in that the following are incorporated:

- o a catalytic system comprising a
5 polyaddition metal catalyst (preferably of
platinum nature) and optionally an
inhibitor;
- o optionally one or more semireinforcing,
nonreinforcing or bulking fillers;
- 10 o optionally water;
- o optionally one or more additives chosen
from pigments, plasticizers, other rheology
modifiers, stabilizers and/or adhesion
promoters.

15 14. Method according to any one of Claims 1
to 12, characterized:

in that a polycondensation SM_2 is used which contains:

- at least one reactive silicone oil C POS
whose crosslinking functional groups Fc
20 react by polycondensation, these C POSSs
corresponding to the following formula (1):



in which:

- * R^1 represents monovalent hydrocarbon
25 radicals which are identical or
different, and Y represents

hydrolysable or condensable groups OR^{11}
 with R^{11} corresponding to the same
 definition as that given above for R^c ,

* n is chosen from 1, 2 and 3 with $n = 1$,
 when $R = H$ is a hydroxyl, and x has a
 sufficient value to confer on the oils
 of formula (1) a dynamic viscosity at
 25°C of between 1 000 and
 200 000 mPa.s,

10 this C POS being intended to react with
 another C POS or with at least one
 crosslinking agent D ,

▪ and/or at least one nonreactive E POS
 different from the C POS(s);

15 and in that the following are incorporated:

- o a catalytic system comprising a
 condensation metal catalyst;
- o optionally one or more semireinforcing,
 nonreinforcing or bulking fillers;
- 20 o optionally water;
- o optionally one or more additives chosen
 from pigments, plasticizers, other rheology
 modifiers, stabilizers and/or adhesion
 promoters.

25 15. Method according to any one of Claims 1
 to 12, characterized in that a polydehydrogeno-
 condensation SM_3 is used which contains:

- at least one C' type POS carrying hydroxyl crosslinking functional groups Fc' and/or OR' functional groups ($R' = C_1-C_{30}$ alkyl, C_2-C_{30} alkenyl, aryl, optionally substituted (preferably halogenated)) precursor of the functional groups Fc' , these crosslinking functional groups Fc' being capable of reacting with other crosslinking functional groups Fb' (SiH) of at least one B' type POS, this C' POS being taken alone or as a mixture with at least one nonreactive (E) POS,
 - at least one reactive silicone oil B' POS, whose crosslinking functional groups Fb' are hydrogen functional groups, this B' POS comprising at least two $\equiv Si-H$ groups per molecule (preferably at least three when the A POS comprises only two $\equiv Si-Vi$ groups per molecule), these $\equiv Si-H$ groups being advantageously present in the chain,
 - and/or at least one nonreactive E POS;
- and in that the following are incorporated:
- o a catalytic system comprising a polydehydrogenocondensation metal catalyst (preferably of platinum nature) and optionally an inhibitor;
 - o optionally one or more semireinforcing,

nonreinforcing or bulking fillers

- o optionally water;
- o optionally one or more additives chosen from pigments, plasticizers, other rheology modifiers, stabilizers and/or adhesion promoters.